JC17 Rec'd PCT/PTO 0 1 JUN 2001

FORM PTO-1390 (REV. 11-2000)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY 'S DOCKET NUMBER: KNI-152-A

U S APPLICATION NO. (If known, see 37 CFR 1 5: 09/857382

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP99/06675	30 November 1999	December3, 1988, April 01, 1999

TITLE OF INVENTION: HYDROPHILIC MEMBER

APPLICANT(S) FOR DO/EO/US: H. Fujimoto, K. Takahashi, K. Takeda, K. Tanaka, E. Ogino, K. Mori, M. Hirata

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [ ] The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   - a. [ ] is attached hereto (required only if not communicated by the International Bureau).
   - b. [XX] has been communicated by the International Bureau.
   - c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   - a. [XX] is attached hereto.
   - b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [X] Amendments to the claims of the International Aplication under PCT Article 19 (35 U.S.C. 371(c)(3))
   - a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   - b. [ ] have been communicated by the International Bureau.
   - c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   - d. [XX] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English lanugage translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [X] A substitute specification. (part of Preliminary Amendment)
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [X] Other items or information:
    International Search Report

JC18 Rec'd PCT/PTO 0 1 JUN 2001

U.S. APPLICATION NO (if known, see 37 CFR 1.5) 09/857382	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER

				CALCULATIONS	PTO USE ONLY
21. [X] The following fees are submitted: **BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):** Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**					
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**					
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**					
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**					
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**					
ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [X] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$ 130.00	
CLAIMS*	NUMBER FILED	NUMBER EXTRA	RATE	$	
Total claims	20 - 20 =		x **$18.00**	$ 0	
Independent claims	1 - 3 =		x **$80.00**	$ 0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$270.00**	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 990.00	
[ ] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. +				$	
* After entry of Preliminary Amendment **SUBTOTAL =**				$	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$	
TOTAL NATIONAL FEE =				$ 990.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$	
TOTAL FEES ENCLOSED =				$ 990.00	
				Amount to be refunded:	$
				charged:	$

a. [X] A check in the amount of $ 990.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. ____________ in the amount of $ __________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0744. A duplicate copy of this sheet is enclosed.

d. [ ] Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Carrier, Blackman & Associates, P.C.
24101 Novi Road, Suite 100
Novi, MI 48375
(248)344-4422
cba@home.msen.com
Customer No. 21828

SIGNATURE

Joseph P. Carrier
NAME

31748
REGISTRATION NUMBER

dated: 01 June 2001

09/857382

JC18 Rec'd PCT/PTO 01 JUN 2001

KNI-152-A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	H. Fujimoto et al.
Serial No.:	Unknown
Filed:	Concurrently Herewith
Group Art Unit:	Unknown
Examiner:	Unknown
Title:	HYDROPHILIC MEMBER

PRELIMINARY AMENDMENT-A

Box Patent Applications
Assistant Commissioner for Patents
Washington, DC 20231

Sir:

In connection with the subject new patent application (filed concurrently herewith), please amend the application as follows.

IN THE SPECIFICATION:

Please amend the specification as shown on the attached sheets (including a clean version of the amended paragraphs and a copy of the original paragraphs showing the changes in hand-written markings).

IN THE CLAIMS:

Please amend claims 1-10 as shown on the attached sheets (including a clean version of the amended paragraphs and a copy of the original paragraphs showing the changes in hand-written markings). Also, please add new claims 11-20 as shown on the attached sheets.

IN THE ABSTRACT:

Please amend Abstract as shown on the attached sheets (including a clean version of the amended drawings and a copy of the drawings showing the changes in hand-written markings).

REMARKS

Upon entry of the present Preliminary Amendment-A the claims in the application are claims 1-20, of which claim 1 is independent.

The specification, claims and abstract have been amended to overcome minor informalities therein, while the claims are also amended to eliminate multiple dependencies therein and to add new claims 11-20. Applicant respectfully submits that all of the above amendments are fully supported by the original application.

Favorable consideration is respectfully requested.

Respectfully submitted,

Joseph P. Carrier
Attorney for Applicant
Registration No. 31,748
(248) 344-4422

Customer No. 21828
Carrier, Blackman & Associates, P.C.
24101 Novi Road, Suite 100
Novi, Michigan 48375
June 01, 2001

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as Express Mail Certificate No. EL699973496US in an envelope addressed to Box Patent Applications, Assistant Commissioner for Patents, Washington, D.C. 20231 on June 01, 2001.

Daniela Peterson

JPC/ms

Initial Information Data Sheet Example 4 (Multiple Inventors with Representation, Continuity and Priority)

Inventor Information

Inventor One Given Name::	Hidefumi
Family Name::	Fujimoto
Postal Address Line One::	c/o Toto Ltd.
Postal Address Line Two::	1-1, Nakashima 2-chome, Kokura-kita-ku, Kita-kyushu-shi
City::	Fukuoka
Country::	Japan
Postal or Zip Code::	
Citizenship Country::	Japan

Inventor Two Given Name::	Kazuo
Family Name::	Takahashi
Postal Address Line One::	c/o Toto Ltd.
Postal Address Line Two::	1-1, Nakashima 2-chome, Kokura-kita-ku, Kita-kyushu-shi
City::	Fukuoka
Country::	Japan
Postal or Zip Code::	
Citizenship Country::	Japan

Inventor Three Given Name::	Koji
Family Name::	Takeda
Postal Address Line One::	c/o Toto Ltd.
Postal Address Line Two::	1-1, Nakashima 2-chome, Kokura-kita-ku, Kita-kyushu-shi
City::	Fukuoka
Country::	Japan
Postal or Zip Code::	
Citizenship Country::	Japan

Inventor Four Given Name::	Keisuke
Family Name::	Tanaka
Postal Address Line One::	c/o Nippon Sheet Glass Co., Ltd.
Postal Address Line Two::	7-28, Kitahama 4-chome, Chuo-ku, Osaka-ku
City::	Osaka
Country::	Japan
Postal or Zip Code::	
Citizenship Country::	Japan

Inventor Five Given Name::	Etsuo
Family Name::	Ogino
Postal Address Line One::	c/o Nippon Sheet Glass Co., Ltd.
Postal Address Line Two::	7-28, Kitahama 4-chome, Chuo-ku, Osaka-ku
City::	Osaka
Country::	Japan

Postal or Zip Code::
Citizenship Country:: Japan

Inventor Six Given Name:: Kenji
Family Name:: Mori
Postal Address Line One:: c/o Nippon Sheet Glass Co., Ltd.
Postal Address Line Two:: 7-28, Kitahama 4-chome, Chuo-ku, Osaka-ku
City:: Osaka
Country:: Japan
Postal or Zip Code::
Citizenship Country:: Japan

Inventor Seven Given Name: Masahiro
Family Name:: Hirata
Postal Address Line One:: c/o Nippon Sheet Glass Co., Ltd.
Postal Address Line Two:: 7-28, Kitahama 4-chome, Chuo-ku, Osaka-ku
City:: Osaka
Country:: Japan
Postal or Zip Code::
Citizenship Country:: Japan

Assignment Information

Rights assigned?:: Yes

Assignee One:: Toto Ltd.
Postal Address Line One:: 1-1, Nakashima 2-chome, Kokura-kita-ku, Kita-kyushu-shi
Postal Address Line Two::
City:: Fukuoka
Country:: Japan
Postal or Zip Code::

Assignee Two: Nippon Sheet Glass Co., Ltd.
Postal Address Line One:: 7-28, Kitahama 4-chome, Chuo-ku, Osaka-shi
Postal Address Line Two::
City:: Osaka
Country:: Japan
Postal or Zip Code::

Correspondence Information

Correspondence Customer No:: 21828
Name Line One:: Joseph P. Carrier
Name Line Two:: Carrier, Blackman & Associates, P.C.

Address Line One:: 24101 Novi Road
Address Line Two:: Suite 100
City:: Novi
State or Province:: MI
Postal or Zip Code:: 48375
Telephone One:: (248)344-4422
Fax:: (248)344-1096
Electronic Mail:: cba@home.msen.com

Application Information

Title Line One:: Hydrophilic Member
Title Line Two::
Total Drawing Sheets:: 1
Formal Drawings?:: yes
Application Type:: Utility
Docket Number:: KNI-152-A
Claims Small Entity Status?:: no

Representative Information

Registration Number 1:: 31,748
Registration Number 2:: 32,397

Continuity Information

This Application Is:: National Phase of International Application
Application One:: PCT/JP99/06675
Filing Date:: 30 November 1999

Priority Information

Foreign Application One:: 10-343688
Filing Date:: 03 December 1998
Country:: Japan
Priority Claimed?:: yes

Foreign Application Two:: 11-95014
Filing Date:: 01 April 1999
Country:: Japan
Priority Claimed?:: yes

APPENDIX B

PTO will send, via Internet Electronic Mail, acknowledgment letter indicating the Application Number, Mail room date and Docket Number (if provided) if the e-mail address is indicated on the Data Entry Format sheet. Note: **By providing an Electronic Mail address application implicitly authorized PTO to send the acknowledgment letter but does not authorize PTO to use the Electronic Mail address for any other communication regarding the application.** See the attached example of the acknowledgment letter below.

COURTESY ACKNOWLEDGMENT OF APPLICATION RECEIPT

Application Serial Number: ____________________

Mailroom Date: ____________________

Docket Number: KNI-152-A

Thank you for using the Patent Application Data Entry Format. The above identified application was received by the U.S. Patent and Trademark Office of the above date and has been imaged captured by the Patent Image Capture System. The above date does NOT represent that a filing date has been granted. A filing date receipt will be sent once an initial formalities examination of the application papers has been completed and all required parts of the application needed for granting of a filing date have been found to be present.

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1/PRTS

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Hydrophilic Member

Technical Field of the Invention

This invention relates to a hydrophilic member and especially to a hydrophilic member having superior hydrophilic restoration properties.

Background Art

Japanese Unexamined Patent Publication Numbers Hei 9-278431, Hei 9-295363, Hei 10-36144, and Hei 10-231146 are known as background art having hydrophilic and anti-fogging properties on the substrate surfaces of glass and the like.

Japanese Unexamined Patent Publication Number Hei 9-278431 discloses the application, on a substrate surface, of a surface treatment agent including phosphoric acids or salts thereof, soluble aluminum compounds, water-soluble silicates, surface active agents, and solvents. The mean surface roughness of the hydrophilic film is 0.5 to 500 nm.

Japanese Unexamined Patent Publication Number Hei 9-295363 discloses a film of titanium oxide or tin oxide formed on a substrate surface, having a mean surface roughness of at least 1 μm.

Japanese Unexamined Patent Publication Number Hei 10-36144 discloses a photocatalyst film such as titanium oxide (TiO_2) formed on a glass substrate surface and a porous inorganic oxide film such as silicon oxide (SiO_2) formed on the surface of the photocatalyst film.

Japanese Unexamined Patent Publication Number Hei 10-231146 discloses an alkali barrier film and a photocatalyst film formed on the surface of a glass substrate. The mean surface roughness of the photocatalyst film is from1.5 to 80 nm.

The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-278431 is not practical since both the chemical durability and wear resistance of the hydrophilic film are low. The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-295363 is not applicable to the surface of a transparent substrate such as a glass plate because the mean surface roughness (Ra) of the hydrophilic film is greater than or equal to 1 μm, preferably greater than or equal to 4 μm, and the transparency thereof is low (high haze). With regards to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-36144, since wear resistance of the hydrophilic film is low because of the porosity thereof, hydrophilic function thereof is lost and is not easily recovered when contamination such as oil enters into the pores. With respect to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-231146, time is needed for production because the hydrophilic film is formed of a plurality of layers.

Moreover, with each of the above-disclosed prior arts, a hydrophilic film is formed on the surface of a substrate and hydrophilic properties are further improved by making the surface have

minute irregularities. However, in the case of a contaminated substrate, there is a drawback of slow restoration of the hydrophilic properties after washing of the substrate surface with a detergent.

For example, since a surface such as that of a windshield or a mirror provided with a lavatory is easily contaminated, it is frequently washed with a detergent. Unfortunately, restoration of hydrophilic properties after washing is slow, leading to minute water drops easily adhering to the surface and anti-fogging properties fade.

Disclosure of the Invention

In order to resolve the problems mentioned above, according to the present invention, there is provided a hydrophilic member, comprising a tin oxide layer formed on a surface of a substrate directly or through an undercoat film in between acting as a barrier against alkali, and an overcoat layer formed on the surface of the tin oxide layer, wherein the overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide. Furthermore, the mean surface roughness (Ra) of the top surface thereof is within a range of from 0.5 to 25 nm.

The mean surface roughness (Ra) is preferably within a range of from 0.5 to 25 nm, more preferably within a range of 5 to 15 nm. The long-term stability of the hydrophilic performance is further improved within this range.

If only a tin oxide (SnO_2) layer is formed on the surface of the substrate and the surface of this tin oxide (SnO_2) layer is rough, hydrophilic properties are displayed, as mentioned in the prior art (Unexamined Patent Publication Number Hei 9-295363). Unfortunately, upon washing the surface once with bath soap, the contact angle with water becomes 70° to 80°.

On the other hand, when a thin film such as a film of silicon oxide (SiO_2) is formed on the surface of the above-mentioned tin oxide (SnO_2) layer, the post-washing contact angle with water becomes less than 10°.

It is conceivable that the reason is because super-hydrophilic properties are present after washing since, from the aspect of surface polarity, tin oxide (SnO_2) and silicon oxide (SiO_2) have opposite polarities and bath soap is anionic.

It is preferable that the above-mentioned tin oxide (SnO_2) has a rutile structure. By making the tin oxide (SnO_2) to have a rutile structure, it is possible to form a polycrystalline thin film having a surface of preferable irregularities.

Moreover, by making the mean surface roughness (R_a) of the tin oxide (SnO_2) to be from 0.5 to 25 nm and transferring these irregularities to the top surface, it is possible to make the mean surface roughness (R_a) of the top surface to be from 0.5 to 25 nm.

It is not preferable that the mean surface roughness (R_a) be less than 0.5 nm, because effective

irregularities which improve long-term maintainability of hydrophilic properties and functions would not be formed. It is also not preferable for the mean surface roughness (R_a) to exceed 25 nm, in which case irregularities would be too great and transparency lost, or the long-term stability of the hydrophilic function would be lowered.

Additionally, it is preferable to make the mean spacing (S_m) of the irregularities to be from 4 to 300 nm. It is not preferable for the mean spacing (S_m) of the irregularities to be either less than 4 nm or greater than 300 nm, which would result in reduction of the long-term stability of hydrophilic performance and anti-fogging performance. The mean spacing (S_m) of the irregularities is more preferably from 5 to 150 nm. Within this range, the long-term stability of hydrophilic performance is further improved.

As a method of indicating the mean surface roughness (R_a), arithmetical mean surface roughness (R_a) as defined by JIS B0601 (1994) is used. The value (nm) of arithmetical mean surface roughness is expressed as "the absolute value of the deviation from the mean line", and is rendered by the following equation 1.

[equation 1] $$Ra = \frac{1}{L}\int_0^L |f(x)|dx$$

L : reference length

f(x) : roughness curve expression taking X-axis in the direction of mean line and Y-axis in the direction of longitudinal magnification of the sampled part

Moreover, the mean spacing of irregularities S_m, too, is defined by JIS B0601 (1994). The arithmetical mean value (nm) of irregularities is expressed as "the mean value of the spacing between cycles of peaks and valleys obtained from the point where the roughness curve and the mean line cross", and is rendered by the following equation 2.

[equation 2] $$Sm = \frac{1}{n}\sum_{i=1}^{n} Smi$$

S_{mi} : spacing of irregularities (nm)

n: number of spacings of irregularities within the reference length

It is preferable for the thickness of the tin oxide film (SnO_2) to be from 10 to 800 nm, and for the thickness of the overcoat layer of silicon oxide film (SiO_2) or the like to be from 0.1 to 100 nm.

When the thickness of the tin oxide is less than or greater than this range, the desired irregularities cannot be obtained. That is, deviation outside of this range is not preferable because,

when the thickness of the tin oxide is smaller than this range, then a film of uniform thickness will not be realized; and when the thickness of the tin oxide is larger than this range, then the spacing of irregularities will become too large.

A film mainly comprised of common silicon oxide is preferable as the undercoat for the alkali barrier. Additives such as P (phosphorous) and B (boron) may be added, and oxide compounds of tin oxide may be used as needed.

The undercoat film for the alkali barrier may be formed using known processes. Examples include the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, and CVD (chemical vapor deposition) method.

It is preferable that the undercoat film for the alkali film be at least 10 nm yet not greater than 300 nm. A thickness less than 10 nm is not preferable because it is insufficient for producing an effective alkali barrier. Additionally, a thickness greater than 300 nm is not preferable because interference colors frequently become noticeable and it becomes difficult to control the optical characteristics of a glass plate.

Glass mainly comprised of silicon oxide (SiO_2), tile, ceramics, or a metal plate is suitable for use as the substrate. Moreover, a hydrophilic member according to the present invention may be applied to mirrors, for example.

Brief Descriptions of the Drawings

Figures 1(a) and 1(b) are, respectively, enlarged cross-sectional views of a hydrophilic member according to the present invention.

Preferred Embodiment to Implement the Invention

Hereinbelow, explanation will be made of the preferred embodiment of the present invention, based upon the attached drawings.

In the embodiment shown in Figure 1(a), the hydrophilic member comprises a film of tin oxide (SnO_2) 2 formed on the surface of a glass plate 1 as a substrate and a film of silicon oxide (SiO_2) 3 as an overcoat layer formed on the surface of this tin oxide (SnO_2) film 2.

In the embodiment shown in Figure 1(b), an undercoat film 4 stands between the glass plate1 and the tin oxide (SnO_2) film 2 to prevent alkalis such as Na from escaping out of the glass plate 1.

In Figure 1, R_a is the mean surface roughness and Sm indicates the mean spacing of the irregularities.

Soda glass, which has SiO_2 as its main component, is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, CVD (chemical vapor deposition) method, or sputtering method. The thickness ranges from 10 to 800

nm and the mean surface roughness (R_a) ranges from 0.5 to 25 nm. The film of tin oxide (SnO_2) 2 has a rutile structure.

The film of silicon oxide (SiO_2) 3 has a thickness ranging from 0.1 through 100 nm and is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, chemical vapor deposition method, or sputtering method. In addition, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide (SnO_2) film 2 are transferred just as they are, and the range of the mean surface roughness (R_a) of the surface of the silicon oxide (SiO_2) film 3 also becomes within the range of 0.5 to 25 nm.

The mean spacing (S_m) of irregularities preferably ranges from 4 to 300 nm. It is not desirable that the spacing deviate from this range because the long-term stability of the hydrophilic properties is low.

By forming minute irregularities on the surface, the hydrophilic properties of the surface can be further improved.

That is, when the surface area becomes larger by r times due to formation of minute irregularities on the surface, $\cos\theta' = r\cos\theta$ ($90° > \theta > \theta'$) is established by Wenzel's formula, in which the contact angle of water at the time of the flat surface is θ and the contact angle of water at the time of forming irregularities is θ'. However, it is not the case when the contact angle θ deviates greatly from 90 degrees.

For example, forming irregularities on the surface of a member having a contact angle of 30° with respect to water when the surface is flat, and taking the surface area to be multiplied 1.1 times, then, from the above equation, $\cos\theta' = 1.1\cos 30° = 0.935$, and from this it is determined that $\theta' = 17.7°$. Similarly, when the surface area is multiplied by 1.15, θ' becomes 5.2°.

However, this equation is not necessarily established when θ is small, however, as a tendency, θ' becomes smaller by the provisions of irregularities.

That is, by the formation of minute irregularities on the surface, the hydrophilic surface becomes all-the-more hydrophilic.

On the other hand, as the undercoat film 4 for an alkali barrier, a thin film with silicon oxide as the main component or a compound oxide film comprised of silicon oxide and tin oxide, a film of silicon oxide which includes carbon, or layers of a film with tin oxide as the main components and a film with silicon oxide as the main component, or the like may be used.

For example, a compound oxide film comprised of silicon oxide and tin oxide or a film of silicon oxide which includes carbon has a refractive index which is between that of the glass plate 1 and the tin oxide film 2. Therefore, an even more preferable appearance can be obtained. That is, by having an undercoat film with an intermediate refractive index, it is possible to control interference color changes (color inconsistencies) arising from irregular thickness of the tin oxide

film, as well as neutralize reflection hues.

In the case where the undercoat film is a layered body of, for example, a film whose main component is tin oxide and a film whose main component is silicon oxide, because the apparent refractive index of the layered body is between the refractive index of the glass plate 1 and the refractive index of the tin oxide film 2 by adjusting the thickness of the respective films, the functions of the above-mentioned undercoat film with an intermediate refractive index can be obtained.

In the case where the hydrophilic member having the above-mentioned structure is applied to a mirror, a thin film of metal, for example, silver, is formed on the rear surface of the glass plate 1, between the glass plate 1 and the undercoat film 4; or, in the case of no undercoat, between the glass plate 1 and tin oxide (SnO_2) film 2.

Next, explanation will be made of processes for the formation of films occurring with the preferred embodiment of the present invention and comparative examples. Specifically, using a film-forming apparatus (not shown), the sample of embodiment 1 was made by forming, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the samples of embodiments 2, 3, 4, and 6 were formed with, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the sample of embodiment 5 was formed with, in order, a film of tin oxide, a film of silicon oxide, a film of tin oxide, and a film of silicon oxide on the surface of a glass plate.

Using the same process as that of embodiment 1, the sample of comparative example 1 was made with, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. The sample of comparative example 2 was made by conducting an etching process on the surface of an ordinary glass plate, in which the glass plate was immersed into an aqueous solution whose main component was hydrosilicofluoric acid, and on the surface of the glass plate were formed minute irregularities comprised of a porous film whose main component was silica. Using the same process as that of embodiment 1, the samples of comparative examples 4 and 5 were made by forming a tin oxide film on the surface of a glass plate.

Next, the mean surface roughness (R_a) and the mean spacing (Sm) of the samples of the embodiments and the comparative examples were measured. These values were calculated from profile curves measured with an atomic force microscope (AFM) or an electron microscope.

Furthermore, the samples were washed with bath soap, and changes in the contact angles were measured so that wetting properties of the sample surface with respect to water could be confirmed. The angle of contact with water was measured immediately after washing, after the elapse of 2 hours, and after the elapse of 200 hours.

Tables 1 and 2, below, are, with regards to the hydrophilic member according to the present invention and the comparative examples, comparisons of changes of the contact angles with water

after washing with a detergent.

Table 1

		Embodiments					
		1	2	3	4	5	6
mean surface roughness (nm)		10.0	3.0	7.0	13.0	25.0	8.5
mean spacing (nm)		40	30	65	110	150	70
change of contact angle (°)	immediately after washing	3.0	5.0	4.0	5.0	10.0	4.0
	2 hours after washing	4.0	10.0	6.0	6.0	12.0	6.0
	200 hours after washing	10.0	25.0	15.0	13.0	16.0	14.0
undercoat film composition		--	SiO_2	SiO_2	SiO_2	SnO_2/SiO_2	SiO_2
undercoat film thickness (nm)		--	20	20	20	25/25	20
SnO_2 film thickness (nm)		350	20	250	600	800	300
overcoat film thickness (nm)		20	20	50	20	50	50
remarks							

Table 2

		Comparative examples*				
		1	2	3	4	5
mean surface roughness (nm)		30.0	5.0	1.0	5.0	7.0
mean spacing (nm)		250	45	∞ (infinite)	50	70
change of contact angle (°)	immediately after washing	57.0	14.0	18.0	70.0	78.0
	2 hours after washing	65.0	18.0	20.0	70.0	79.0
	200 hours after washing	68.0	32.0	41.0	73.0	80.0
undercoat film composition		SnO_2/SiO_2	--	--	--	--
undercoat film thickness (nm)		25/25	--	--	--	--
SnO_2 film thickness (nm)		1000	--	--	60	150
overcoat film thickness (nm)		--	--	--	--	--
remarks		*Comparative example 2: glass plate on the surface of which are minute irregularities formed by etching Comparative example 3: ordinary glass plate Comparative example 4: glass plate with a film of tin oxide (SnO_2) provided on the surface Comparative example 5: glass plate with a film of tin oxide (SnO_2) provided on the surface				

Table 1 clearly shows that a hydrophilic member according to the present invention has an angle of contact with water of 10° or less just after washing, and the hydrophilic properties are durable over long periods of time.

On the other hand, Table 2 clearly shows that a common glass plates (comparative example 3) has an angle of contact with water of about 10° after washing, but the angle of contact gradually increases with time. This may be considered due to hydrophilic durability not being attained since the surface irregularities are small ($R_a \fallingdotseq 1$nm). A glass plate with fine irregularities formed on the surface by etching (comparative example 2) also has a contact angle with water of about 10°, but the angle of contact gradually increases with the elapse of time. This is presumably due to durability worsening because the spacing of irregularities is too small in relation to the surface irregularities, and the hydrophilic functions decreasing over time.

Moreover, in the case where the thickness of the tin oxide (SnO_2) film exceeds the range of the present invention (comparative example 1), since the spacing of irregularities on the surface becomes large (S_m > 300 nm), the spacing of irregularities on the surface of the silicon oxide film (SiO_2) becomes large, resulting in hydrophilic properties not able to be attained. Furthermore, when a film of tin oxide (SnO_2) only is formed on a glass plate (comparative examples 4 and 5), the angle of contact with water after washing is 70° or greater and hydrophilic properties are not manifested, regardless of the thickness of the tin oxide film (SnO_2). This is presumably due to the nature of the tin oxide (SnO_2) film itself, regardless of the surface shape.

Embodiment 6 is a mirror formed with a film of the same composition as comparative example 3 on the surface of a glass plate having a silvered rear surface. This mirror surface does not fog at all, even when breath is exhaled thereupon, the angle of contact with water becomes 10° or less just after washing, and it maintains hydrophilic properties over long periods. Accordingly, the mirror of embodiment 6 has high hydrophilic properties, and exhibits desirable hydrophilic retention properties.

Industrial applicability

As explained above, according to the first aspect of the above-mentioned hydrophilic member, the angle of contact with respect to water becomes small, allowing still greater long-term stability of hydrophilic properties to be obtained.

According to the second aspect of the above-mentioned hydrophilic member, it is possible to form a polycrystalline film having a desirably irregular surface, while attaining the effects of the above-mentioned first aspect.

According to the third aspect of the above-mentioned hydrophilic member, while attaining the effects of the above-mentioned first and second aspects, hydrophilic effects occurring on the top surface can be sufficiently attained, yet recovery of hydrophilic properties after washing will occur

within an extremely short period of time, and the retention of the hydrophilic properties is high.

According to the fourth aspect of the above hydrophilic members, it is possible to maintain hydrophilic properties over a long period of time, while attaining the respective effects of any one of the above-mentioned first, second, or third aspects.

According to the fifth aspect of the above-mentioned hydrophilic member, it is possible to form a desired hydrophilic film while attaining the respective effects of any one of the above-mentioned first through fourth aspects.

According to the sixth aspect of the above-mentioned hydrophilic member, it is possible to obtain desired irregularities while attaining the respective effects of any one of the above-mentioned first through fifth aspects.

According to the seventh aspect of the above-mentioned hydrophobic member, while attaining the respective effects of any one of the above-mentioned first through sixth aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the refractive index of the undercoat film is between the refractive index of the glass plate and the tin oxide film.

According to the eighth aspect of the above-mentioned hydrophilic members, while attaining the respective effects of any one of the above-mentioned first through seventh aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the apparent refractive index of the layered film is between the refractive index of the glass plate and the tin oxide film.

According to the ninth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through eighth aspects, it is possible to make effective applications to mirrors, windshields, anti-fogging/anti-fouling glass for construction, spectacles, lenses, tile, metal plates, and the like.

According to the tenth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through ninth aspects, it is possible to make effective applications to automobile door mirrors, bathroom mirrors, and the like.

What is claimed is:

1. A hydrophilic member comprising:

a tin oxide layer formed on a surface of a substrate directly or through an undercoat film acting as a barrier against alkali and;

an overcoat layer formed on the surface of said tin oxide layer, wherein said overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide, and the mean surface roughness (R_a) of the top surface thereof is within a range of 0.5 to 25 nm.

2. A hydrophilic member according to claim 1, wherein said tin oxide (SnO_2) has a rutile structure.

3. A hydrophilic member according to either of claim 1 or claim 2, wherein the mean surface roughness (R_a) of said tin oxide (SnO_2) is within a range of from 0.5 to 25 nm, and thereby the mean surface roughness (R_a) of the top surface is within a range of 0.5 to 25 nm.

4. A hydrophilic member according to any one of claims 1 through 3, wherein the mean spacing (S_m) of the irregularities of the top surface is within a range of 4 nm to 300 nm.

5. A hydrophilic member according to any one of claims 1 through 4, wherein said tin oxide layer has a thickness of within a range of 10 to 800 nm.

6. A hydrophilic member according to any one of claims 1 through 5, wherein said overcoat layer has a thickness of within a range of 0.1 to 100nm.

7. A hydrophilic member according to any one of claims 1 through 6, wherein the refractive index of said undercoat film acting as a barrier against alkali is between the refractive index of the substrate and the refractive index of the tin oxide.

8. A hydrophilic member according to any one of claims 1 through 7, wherein said undercoat film is a layered body of tin oxide and silicon oxide.

9. A hydrophilic member according to one of claims 1 through 8, wherein said substrate is glass the main component of which is silicon oxide; tile; ceramic; or a metal plate.

10. A hydrophilic member according to any one of claims 1 through 9, wherein said hydrophilic member is a mirror having a thin metal film formed on the rear surface thereof, between the substrate and the tin oxide layer, or between the undercoat film and the tin oxide layer.

Abstract

A hydrophilic member is provided wherein the restoration of hydrophilic properties after washing occurs in an extremely short amount of time, yet the retention effect of the recovered hydrophilic properties is high. On the surface of glass plate 1, which is used as a substrate, is formed a tin oxide (SnO_2) film 2, and on the surface of this tin oxide (SnO_2) film 2 is formed, as an overcoat layer, a silicon oxide (SiO_2) film 3. Soda glass which has SiO_2 as its main component is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed, for example, by the chemical vapor deposition method, the thickness of the film being from 10 to 800 nm and the mean surface roughness (R_a) of the surface being from 0.5 through 25nm. Furthermore, the silicon oxide (SiO_2) film 3 is formed by the sputtering method, the thickness being from 0.1 to 100 nm. Moreover, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide film (SnO_2) 2 are transferred just as they are, which makes the silicon oxide (SiO_2) film have a mean surface roughness (R_a) of from 0.5 through 25 nm.

Hydrophilic Member

BACKGROUND OF THE INVENTION

Technical Field of the Invention

This invention relates to a hydrophilic member and especially to a hydrophilic member having superior hydrophilic restoration properties.

~~Background~~ Description of Relevant Art

Japanese Unexamined Patent Publication Numbers Hei 9-278431, Hei 9-295363, Hei 10-36144, and Hei 10-231146 are known as background art having hydrophilic and anti-fogging properties on the substrate surfaces of glass and the like.

Japanese Unexamined Patent Publication Number Hei 9-278431 discloses the application, on a substrate surface, of a surface treatment agent including phosphoric acids or salts thereof, soluble aluminum compounds, water-soluble silicates, surface active agents, and solvents. The mean surface roughness of the hydrophilic film is 0.5 to 500 nm.

Japanese Unexamined Patent Publication Number Hei 9-295363 discloses a film of titanium oxide or tin oxide formed on a substrate surface, having a mean surface roughness of at least 1 μm.

Japanese Unexamined Patent Publication Number Hei 10-36144 discloses a photocatalyst film such as titanium oxide (TiO_2) formed on a glass substrate surface and a porous inorganic oxide film such as silicon oxide (SiO_2) formed on the surface of the photocatalyst film.

Japanese Unexamined Patent Publication Number Hei 10-231146 discloses an alkali barrier film and a photocatalyst film formed on the surface of a glass substrate. The mean surface roughness of the photocatalyst film is from1.5 to 80 nm.

The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-278431 is not practical since both the chemical durability and wear resistance of the hydrophilic film are low. The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-295363 is not applicable to the surface of a transparent substrate such as a glass plate because the mean surface roughness (Ra) of the hydrophilic film is greater than or equal to 1 μm, preferably greater than or equal to 4 μm, and the transparency thereof is low (high haze). With regards to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-36144, since wear resistance of the hydrophilic film is low because of the porosity thereof, hydrophilic function thereof is lost and is not easily recovered when contamination such as oil enters into the pores. With respect to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-231146, time is needed for production because the hydrophilic film is formed of a plurality of layers.

Moreover, with each of the above-disclosed ~~prior~~ background arts, a hydrophilic film is formed on the surface of a substrate and hydrophilic properties are further improved by making the surface have

minute irregularities. However, in the case of a contaminated substrate, there is a drawback of slow restoration of the hydrophilic properties after washing of the substrate surface with a detergent.

For example, since a surface such as that of a windshield or a mirror provided with a lavatory is easily contaminated, it is frequently washed with a detergent. Unfortunately, restoration of hydrophilic properties after washing is slow, leading to minute water drops easily adhering to the surface and anti-fogging properties fade.

Summary

Disclosure of the Invention

In order to resolve the problems mentioned above, according to the present invention, there is provided a hydrophilic member, comprising a tin oxide layer formed on a surface of a substrate directly or through an undercoat film in between acting as a barrier against alkali, and an overcoat layer formed on the surface of the tin oxide layer, wherein the overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide. Furthermore, the mean surface roughness (Ra) of the top surface thereof is within a range of from 0.5 to 25 nm.

The mean surface roughness (Ra) is preferably within a range of from 0.5 to 25 nm, more preferably within a range of 5 to 15 nm. The long-term stability of the hydrophilic performance is further improved within this range.

If only a tin oxide (SnO_2) layer is formed on the surface of the substrate and the surface of this tin oxide (SnO_2) layer is rough, hydrophilic properties are displayed, as mentioned in the prior art (Unexamined Patent Publication Number Hei 9-295363). Unfortunately, upon washing the surface once with bath soap, the contact angle with water becomes 70° to 80°.

On the other hand, when a thin film such as a film of silicon oxide (SiO_2) is formed on the surface of the above-mentioned tin oxide (SnO_2) layer, the post-washing contact angle with water becomes less than 10°.

It is conceivable that the reason is because super-hydrophilic properties are present after washing since, from the aspect of surface polarity, tin oxide (SnO_2) and silicon oxide (SiO_2) have opposite polarities and bath soap is anionic.

It is preferable that the above-mentioned tin oxide (SnO_2) layer has a rutile structure. By making the tin oxide (SnO_2) to have a rutile structure, it is possible to form a polycrystalline thin film having a surface of preferable irregularities.

Moreover, by making the mean surface roughness (R_a) of the tin oxide (SnO_2) layer to be from 0.5 to 25 nm and transferring these irregularities to the top surface, it is possible to make the mean surface roughness (R_a) of the top surface to be from 0.5 to 25 nm.

It is not preferable that the mean surface roughness (R_a) be less than 0.5 nm, because effective

irregularities which improve long-term maintainability of hydrophilic properties and functions would not be formed. It is also not preferable for the mean surface roughness (R_a) to exceed 25 nm, in which case irregularities would be too great and transparency lost, or the long-term stability of the hydrophilic function would be lowered.

Additionally, it is preferable to make the mean spacing (S_m) of the irregularities to be from 4 to 300 nm. It is not preferable for the mean spacing (S_m) of the irregularities to be either less than 4 nm or greater than 300 nm, which would result in reduction of the long-term stability of hydrophilic performance and anti-fogging performance. The mean spacing (S_m) of the irregularities is more preferably from 5 to 150 nm. Within this range, the long-term stability of hydrophilic performance is further improved.

As a method of indicating the mean surface roughness (R_a), arithmetical mean surface roughness (R_a) as defined by JIS B0601 (1994) is used. The value (nm) of arithmetical mean surface roughness is expressed as "the absolute value of the deviation from the mean line", and is rendered by the following equation 1.

[equation 1] $$Ra = \frac{1}{L}\int_0^L |f(x)|dx$$

L : reference length

f(x) : roughness curve expression taking X-axis in the direction of mean line and Y-axis in the direction of longitudinal magnification of the sampled part

Moreover, the mean spacing of irregularities S_m, too, is defined by JIS B0601 (1994). The arithmetical mean value (nm) of irregularities is expressed as "the mean value of the spacing between cycles of peaks and valleys obtained from the point where the roughness curve and the mean line cross", and is rendered by the following equation 2.

[equation 2] $$Sm = \frac{1}{n}\sum_{i=1}^{n} Smi$$

S_{mi} : spacing of irregularities (nm)

n: number of spacings of irregularities within the reference length

It is preferable for the thickness of the tin oxide film or layer (SnO_2) to be from 10 to 800 nm, and for the thickness of the overcoat layer of silicon oxide film (SiO_2) or the like to be from 0.1 to 100 nm.

When the thickness of the tin oxide is less than or greater than this range, the desired irregularities cannot be obtained. That is, deviation outside of this range is not preferable because,

when the thickness of the tin oxide is smaller than this range, then a film of uniform thickness will not be realized; and when the thickness of the tin oxide is larger than this range, then the spacing of irregularities will become too large.

A film mainly comprised of common silicon oxide is preferable as the undercoat for the alkali barrier. Additives such as P (phosphorous) and B (boron) may be added, and oxide compounds of tin oxide may be used as needed.

The undercoat film for the alkali barrier may be formed using known processes. Examples include the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, and CVD (chemical vapor deposition) method.

It is preferable that the undercoat film for the alkali ~~film~~ barrier be at least 10 nm yet not greater than 300 nm. A thickness less than 10 nm is not preferable because it is insufficient for producing an effective alkali barrier. Additionally, a thickness greater than 300 nm is not preferable because interference colors frequently become noticeable and it becomes difficult to control the optical characteristics of a glass plate.

Glass mainly comprised of silicon oxide (SiO_2), tile, ceramics, or a metal plate is suitable for use as the substrate. Moreover, a hydrophilic member according to the present invention may be applied to mirrors, for example.

Brief Descriptions of the Drawings

Figures 1(a) and 1(b) are, respectively, enlarged cross-sectional views of a hydrophilic members according to the present invention, the member of Fig. 1(b) including an undercoat film not included in the member of Fig. 1(a).

Detailed Description of Preferred Embodiment to Implement the Invention

Hereinbelow, explanation will be made of the preferred embodiments of the present invention, based upon the attached drawings.

In the embodiment shown in Figure 1(a), the hydrophilic member comprises a film of tin oxide (SnO_2) 2 formed on the surface of a glass plate 1 as a substrate and a film of silicon oxide (SiO_2) 3 as an overcoat layer formed on the surface of this tin oxide (SnO_2) film 2.

In the embodiment shown in Figure 1(b), an undercoat film 4 stands between the glass plate1 and the tin oxide (SnO_2) film 2 to prevent alkalis such as Na from escaping out of the glass plate 1.

In Figure 1, R_a is the mean surface roughness and Sm indicates the mean spacing of the irregularities.

Soda glass, which has SiO_2 as its main component, is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, CVD (chemical vapor deposition) method, or sputtering method. The thickness ranges from 10 to 800

nm and the mean surface roughness (R_a) ranges from 0.5 to 25 nm. The film of tin oxide (SnO_2) 2 has a rutile structure.

The film of silicon oxide (SiO_2) 3 has a thickness ranging from 0.1 through 100 nm and is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, chemical vapor deposition method, or sputtering method. In addition, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide (SnO_2) film 2 are transferred just as they are, and the range of the mean surface roughness (R_a) of the surface of the silicon oxide (SiO_2) film 3 also becomes within the range of 0.5 to 25 nm.

The mean spacing (S_m) of irregularities preferably ranges from 4 to 300 nm. It is not desirable that the spacing deviate from this range because the long-term stability of the hydrophilic properties is low ~~.~~ outside of the range

By forming minute irregularities on the surface, the hydrophilic properties of the surface can be further improved.

That is, when the surface area becomes larger by r times due to formation of minute irregularities on the surface, $\cos\theta' = r\cos\theta$ ($90° > \theta > \theta'$) is established by Wenzel's formula, in which the contact angle of water at the time of the flat surface is θ and the contact angle of water at the time of forming irregularities is θ'. However, it is not the case when the contact angle θ deviates greatly from 90 degrees.

For example, forming irregularities on the surface of a member having a contact angle of 30° with respect to water when the surface is flat, and taking the surface area to be multiplied 1.1 times, then, from the above equation, $\cos\theta' = 1.1\cos 30° = 0.935$, and from this it is determined that $\theta' = 17.7°$. Similarly, when the surface area is multiplied by 1.15, θ' becomes 5.2°.

However, this equation is not necessarily established when θ is small, however, as a tendency, θ' becomes smaller by the provisions of irregularities.

That is, by the formation of minute irregularities on the surface, the hydrophilic surface becomes all-the-more hydrophilic.

On the other hand, as the undercoat film 4 for an alkali barrier, a thin film with silicon oxide as the main component or a compound oxide film comprised of silicon oxide and tin oxide, a film of silicon oxide which includes carbon, or layers of a film with tin oxide as the main components and a film with silicon oxide as the main component, or the like may be used.

For example, a compound oxide film comprised of silicon oxide and tin oxide or a film of silicon oxide which includes carbon has a refractive index which is between that of the glass plate 1 and the tin oxide film 2. Therefore, an even more preferable appearance can be obtained. That is, by having an undercoat film with an intermediate refractive index, it is possible to control interference color changes (color inconsistencies) arising from irregular thickness of the tin oxide

film, as well as neutralize reflection hues.

In the case where the undercoat film is a layered body of, for example, a film whose main component is tin oxide and a film whose main component is silicon oxide, because the apparent refractive index of the layered body is between the refractive index of the glass plate 1 and the refractive index of the tin oxide film 2 by adjusting the thickness of the respective films, the functions of the above-mentioned undercoat film with an intermediate refractive index can be obtained.

In the case where the hydrophilic member having the above-mentioned structure is applied to a mirror, a thin film of metal, for example, silver, is formed on the rear surface of the glass plate 1, between the glass plate 1 and the undercoat film 4; or, in the case of no undercoat, between the glass plate 1 and tin oxide (SnO_2) film 2.

Next, explanation will be made of processes for the formation of films occurring with the preferred embodiment s of the present invention and comparative examples. Specifically, using a film-forming apparatus (not shown), [the] a sample of embodiment 1 was made by forming, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the samples [of embodiments] 2, 3, 4, and 6 ~~were formed with,~~ of embodiment 2 in order, a film of silicon oxide, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, [the sample of] embodiment 5 sample was formed with, in order, a film of tin oxide, a film of silicon oxide, a film of tin oxide, and a film of silicon oxide on the surface of a glass plate.

Using the same process as that of embodiment 1, the sample of comparative example 1 was made with, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. The sample of comparative example 2 was made by conducting an etching process on the surface of an ordinary glass plate, in which the glass plate was immersed into an aqueous solution whose main component was hydrosilicofluoric acid, and on the surface of the glass plate were formed minute irregularities comprised of a porous film whose main component was silica. Using the same process as that of embodiment 1, the samples of comparative examples 4 and 5 were made by forming a tin oxide film on the surface of a glass plate. Comparative example 3 is an ordinary glass plate,

Next, the mean surface roughness (R_a) and the mean spacing (Sm) of the samples of the embodiments and the comparative examples were measured. These values were calculated from profile curves measured with an atomic force microscope (AFM) or an electron microscope.

Furthermore, the samples were washed with bath soap, and changes in the contact angles were measured so that wetting properties of the sample surface with respect to water could be confirmed. The angle of contact with water was measured immediately after washing, after the elapse of 2 hours, and after the elapse of 200 hours.

Tables 1 and 2, below, are, with regards to the hydrophilic member according to the present invention and the comparative examples, comparisons of changes of the contact angles with water

after washing with a detergent.

Table 1

		Embodiment[s] Samples					
		1	2	3	4	5	6
mean surface roughness (nm)		10.0	3.0	7.0	13.0	25.0	8.5
mean spacing (nm)		40	30	65	110	150	70
change of contact angle (°)	immediately after washing	3.0	5.0	4.0	5.0	10.0	4.0
	2 hours after washing	4.0	10.0	6.0	6.0	12.0	6.0
	200 hours after washing	10.0	25.0	15.0	13.0	16.0	14.0
undercoat film composition		--	SiO_2	SiO_2	SiO_2	SnO_2/SiO_2	SiO_2
undercoat film thickness (nm)		--	20	20	20	25/25	20
SnO_2 film thickness (nm)		350	20	250	600	800	300
overcoat film thickness (nm)		20	20	50	20	50	50
remarks							

Table 2

		Comparative examples*				
		1	2	3	4	5
mean surface roughness (nm)		30.0	5.0	1.0	5.0	7.0
mean spacing (nm)		250	45	∞ (infinite)	50	70
change of contact angle (°)	immediately after washing	57.0	14.0	18.0	70.0	78.0
	2 hours after washing	65.0	18.0	20.0	70.0	79.0
	200 hours after washing	68.0	32.0	41.0	73.0	80.0
undercoat film composition		SnO_2/SiO_2	--	--	--	--
undercoat film thickness (nm)		25/25	--	--	--	--
SnO_2 film thickness (nm)		1000	--	--	60	150
overcoat film thickness (nm)		--	--	--	--	--
remarks		*Comparative example 2; glass plate on the surface of which are minute irregularities formed by etching Comparative example 3: ordinary glass plate Comparative example 4: glass plate with a film of tin oxide (SnO_2) provided on the surface Comparative example 5: glass plate with a film of tin oxide (SnO_2) provided on the surface				

Table 1 clearly shows that a hydrophilic member according to the present invention has an angle of contact with water of 10° or less just after washing, and the hydrophilic properties are durable over long periods of time.

On the other hand, Table 2 clearly shows that a common glass plates (comparative example 3) has an angle of contact with water of about 10° after washing, but the angle of contact gradually increases with time. This may be considered due to hydrophilic durability not being attained since the surface irregularities are small ($R_a \fallingdotseq 1nm$). A glass plate with fine irregularities formed on the surface by etching (comparative example 2) also has a contact angle with water of about 10°, but the angle of contact gradually increases with the elapse of time. This is presumably due to durability worsening because the spacing of irregularities is too small in relation to the surface irregularities, and the hydrophilic functions decreasing over time.

Moreover, in the case where the thickness of the tin oxide (SnO_2) film exceeds the range of the present invention (comparative example 1), since the spacing of irregularities on the surface becomes large ($S_m > 300$ nm), the spacing of irregularities on the surface of the silicon oxide film (SiO_2) becomes large, resulting in hydrophilic properties not able to be attained. Furthermore, when a film of tin oxide (SnO_2) only is formed on a glass plate (comparative examples 4 and 5), the angle of contact with water after washing is 70° or greater and hydrophilic properties are not manifested, regardless of the thickness of the tin oxide film (SnO_2). This is presumably due to the nature of the tin oxide (SnO_2) film itself, regardless of the surface shape.

Embodiment 6 Sample is a mirror formed with a film of nearly ~~the same~~ composition as comparative example 3 Embodiment sample on the surface of a glass plate having a silvered rear surface. This mirror surface does not fog at all, even when breath is exhaled thereupon, the angle of contact with water becomes 10° or less just after washing, and it maintains hydrophilic properties over long periods. Accordingly, the mirror of embodiment 6 has high hydrophilic properties, and exhibits desirable hydrophilic retention properties.

, i.e. the film characterist are all the same, except that the SnO_2 film thickness is 300nm, rather than 250 nm

Industrial applicability

As explained above, according to the first aspect of the above-mentioned hydrophilic member, the angle of contact with respect to water becomes small, allowing still greater long-term stability of hydrophilic properties to be obtained.

According to the second aspect of the above-mentioned hydrophilic member, it is possible to form a polycrystalline film having a desirably irregular surface, while attaining the effects of the above-mentioned first aspect.

According to the third aspect of the above-mentioned hydrophilic member, while attaining the effects of the above-mentioned first and second aspects, hydrophilic effects occurring on the top surface can be sufficiently attained, yet recovery of hydrophilic properties after washing will occur

within an extremely short period of time, and the retention of the hydrophilic properties is high.

According to the fourth aspect of the above hydrophilic members, it is possible to maintain hydrophilic properties over a long period of time, while attaining the respective effects of any one of the above-mentioned first, second, or third aspects.

According to the fifth aspect of the above-mentioned hydrophilic member, it is possible to form a desired hydrophilic film while attaining the respective effects of any one of the above-mentioned first through fourth aspects.

According to the sixth aspect of the above-mentioned hydrophilic member, it is possible to obtain desired irregularities while attaining the respective effects of any one of the above-mentioned first through fifth aspects.

According to the seventh aspect of the above-mentioned hydrophobic member, while attaining the respective effects of any one of the above-mentioned first through sixth aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the refractive index of the undercoat film is between the refractive index /indices of the glass plate and the tin oxide film.

According to the eighth aspect of the above-mentioned hydrophilic members, while attaining the respective effects of any one of the above-mentioned first through seventh aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the apparent refractive index of the layered film is between the refractive index /indices of the glass plate and the tin oxide film.

According to the ninth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through eighth aspects, it is possible to make effective applications to mirrors, windshields, anti-fogging/anti-fouling glass for construction, spectacles, lenses, tile, metal plates, and the like.

According to the tenth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through ninth aspects, it is possible to make effective applications to automobile door mirrors, bathroom mirrors, and the like.

Although there have been described what are the present embodiments of the invention, it will be understood by persons skilled in the art that variations and modifications may be made thereto without departing from the gist, spirit or essence of the invention. The scope of the invention is indicated by the appended claims,

What is claimed is:

1. A hydrophilic member comprising:

a tin oxide layer formed on a surface of a substrate directly or through an undercoat film acting as a barrier against alkali and; and

an overcoat layer formed on the surface of said tin oxide layer, wherein said overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide, and the mean surface roughness (R_a) of the top surface thereof is within a range of 0.5 to 25 nm.

2. A hydrophilic member according to claim 1, wherein said tin oxide (SnO_2) layer has a rutile structure.

3. A hydrophilic member according to layer either of claim 1 or claim 2, wherein the mean surface roughness (R_a) of said tin oxide (SnO_2) is within a range of from 0.5 to 25 nm, and thereby the mean surface roughness (R_a) of the top surface is also within a range of 0.5 to 25 nm.

4. A hydrophilic member according to any one of claims 1 through 3 claim 1, wherein the mean spacing (S_m) of the irregularities of the top surface of said overcoat layer is within a range of 4 nm to 300 nm.

5. A hydrophilic member according to any one of claims 1 through 4 claim 1, wherein said tin oxide layer has a thickness of within a range of 10 to 800 nm.

6. A hydrophilic member according to any one of claims 1 through 5 claim 1, wherein said overcoat layer has a thickness of within a range of 0.1 to 100nm.

7. A hydrophilic member according to any one of claims 1 through 6 claim 12, wherein the refractive index of said undercoat film acting as a barrier against alkali is between the refractive index of the substrate and the refractive index of the tin oxide layer.

8. A hydrophilic member according to any one of claims 1 through 7 claim 12, wherein said undercoat film is a layered body of tin oxide and silicon oxide.

9. A hydrophilic member according to one of claims 1 through 8 claim 1, wherein said substrate is selected from the group consisting of: glass the main component of which is silicon oxide; tile; ceramic; or and a metal plate.

Claim 1

10. A hydrophilic member according to any one of claims 1 through 9, wherein said hydrophilic member is a mirror having a thin metal film formed on the rear surface thereof, between the substrate and the tin oxide layer, or between the undercoat film and the tin oxide layer.

11. A hydrophilic member according to Claim 1, wherein said overcoat layer is formed directly on the surface of the substrate.

12. A hydrophilic member according to claim 1, further including an undercoat film disposed between the surface of said substrate and said tin oxide layer, said undercoat film acting as a barrier against alkali.

13. A hydrophilic member according to Claim 12, wherein said hydrophilic member is a mirror having a thin metal film formed on the surface thereof, between the undercoat film and the tin oxide layer.

Abstract

A hydrophilic member is provided wherein the restoration of hydrophilic properties after washing occurs in an extremely short amount of time, yet the retention effect of the recovered hydrophilic properties is high. On the surface of glass plate 1, which is used as a substrate, is formed a tin oxide (SnO_2) film 2, and on the surface of this tin oxide (SnO_2) film 2 is formed, as an overcoat layer, a silicon oxide (SiO_2) film 3. Soda glass which has SiO_2 as its main component is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed, for example, by the chemical vapor deposition method, the thickness of the film being from 10 to 800 nm and the mean surface roughness (R_a) of the surface being from 0.5 through 25nm. Furthermore, the silicon oxide (SiO_2) film 3 is formed by the sputtering method, the thickness being from 0.1 to 100 nm. Moreover, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide film (SnO_2) 2 are transferred just as they are, which makes the silicon oxide (SiO_2) film have a mean surface roughness (R_a) of from 0.5 through 25 nm.

corresponding

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Hydrophilic Member

Background of the Invention

1. Technical Field of the Invention

This invention relates to a hydrophilic member and especially to a hydrophilic member having superior hydrophilic restoration properties.

2. Description of Relevant Art

Japanese Unexamined Patent Publication Numbers Hei 9-278431, Hei 9-295363, Hei 10-36144, and Hei 10-231146 are known as background art having hydrophilic and anti-fogging properties on the substrate surfaces of glass and the like.

Japanese Unexamined Patent Publication Number Hei 9-278431 discloses the application, on a substrate surface, of a surface treatment agent including phosphoric acids or salts thereof, soluble aluminum compounds, water-soluble silicates, surface-active agents, and solvents. The mean surface roughness of the hydrophilic film is 0.5 to 500 nm.

Japanese Unexamined Patent Publication Number Hei 9-295363 discloses a film of titanium oxide or tin oxide formed on a substrate surface, having a mean surface roughness of at least 1 μm.

Japanese Unexamined Patent Publication Number Hei 10-36144 discloses a photocatalyst film such as titanium oxide (TiO_2) formed on a glass substrate surface and a porous inorganic oxide film such as silicon oxide (SiO_2) formed on the surface of the photocatalyst film.

Japanese Unexamined Patent Publication Number Hei 10-231146 discloses an alkali barrier film and a photocatalyst film formed on the surface of a glass substrate. The mean surface roughness of the photocatalyst film is from1.5 to 80 nm.

The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-278431 is not practical since both the chemical durability and wear resistance of the hydrophilic

film are low. The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-295363 is not applicable to the surface of a transparent substrate such as a glass plate because the mean surface roughness (Ra) of the hydrophilic film is greater than or equal to 1 μm, preferably greater than or equal to 4 μm, and the transparency thereof is low (high haze). With regards to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-36144, since wear resistance of the hydrophilic film is low because of the porosity thereof, hydrophilic function thereof is lost and is not easily recovered when contamination such as oil enters into the pores. With respect to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-231146, time is needed for production because the hydrophilic film is formed of a plurality of layers.

Moreover, with each of the above-disclosed background arts, a hydrophilic film is formed on the surface of a substrate and hydrophilic properties are further improved by making the surface have minute irregularities. However, in the case of a contaminated substrate, there is a drawback of slow restoration of the hydrophilic properties after washing of the substrate surface with a detergent.

For example, since a surface such as that of a windshield or a mirror provided with a lavatory is easily contaminated, it is frequently washed with a detergent. Unfortunately, restoration of hydrophilic properties after washing is slow, leading to minute water drops easily adhering to the surface and anti-fogging properties fade.

Summary of the Invention

In order to resolve the problems mentioned above, according to the present invention, there is provided a hydrophilic member, comprising a tin oxide layer formed on a surface of a substrate directly or through an undercoat film in between acting as a barrier against alkali, and an overcoat layer formed on the surface of the tin oxide layer, wherein the overcoat layer is selected from at

least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide. Furthermore, the mean surface roughness (R_a) of the top surface thereof is within a range of from 0.5 to 25 nm.

The mean surface roughness (R_a) is preferably within a range of from 0.5 to 25 nm, more preferably within a range of 5 to 15 nm. The long-term stability of the hydrophilic performance is further improved within this range.

If only a tin oxide (SnO_2) layer is formed on the surface of the substrate and the surface of this tin oxide (SnO_2) layer is rough, hydrophilic properties are displayed, as mentioned in Unexamined Patent Publication Number Hei 9-295363. Unfortunately, upon washing the surface once with bath soap, the contact angle with water becomes 70° to 80°.

On the other hand, when a thin film such as a film of silicon oxide (SiO_2) is formed on the surface of the above-mentioned tin oxide (SnO_2) layer, the post-washing contact angle with water becomes less than 10°.

It is conceivable that the reason is because super-hydrophilic properties are present after washing since, from the aspect of surface polarity, tin oxide (SnO_2) and silicon oxide (SiO_2) have opposite polarities and bath soap is anionic.

It is preferable that the above-mentioned tin oxide (SnO_2) layer has a rutile structure. By making the tin oxide (SnO_2) to have a rutile structure, it is possible to form a polycrystalline thin film having a surface of preferable irregularities.

Moreover, by making the mean surface roughness (R_a) of the tin oxide (SnO_2) layer to be from 0.5 to 25 nm and transferring these irregularities to the top surface, it is possible to make the mean surface roughness (R_a) of the top surface to be from 0.5 to 25 nm.

It is not preferable that the mean surface roughness (R_a) be less than 0.5 nm, because effective irregularities which improve long-term maintainability of hydrophilic properties and functions

would not be formed. It is also not preferable for the mean surface roughness (R_a) to exceed 25 nm, in which case irregularities would be too great and transparency lost, or the long-term stability of the hydrophilic function would be lowered.

Additionally, it is preferable to make the mean spacing (S_m) of the irregularities to be from 4 to 300 nm. It is not preferable for the mean spacing (S_m) of the irregularities to be either less than 4 nm or greater than 300 nm, which would result in reduction of the long-term stability of hydrophilic performance and anti-fogging performance. The mean spacing (S_m) of the irregularities is more preferably from 5 to 150 nm. Within this range, the long-term stability of hydrophilic performance is further improved.

As a method of indicating the mean surface roughness (R_a), arithmetical mean surface roughness (R_a) as defined by JIS B0601 (1994) is used. The value (nm) of arithmetical mean surface roughness is expressed as "the absolute value of the deviation from the mean line", and is rendered by the following equation 1.

[equation 1] $$Ra = \frac{1}{L}\int_0^L |f(x)|dx$$

L : reference length

f(x) : roughness curve expression taking X-axis in the direction of mean line and Y-axis in the direction of longitudinal magnification of the sampled part

Moreover, the mean spacing of irregularities S_m, too, is defined by JIS B0601 (1994). The arithmetical mean value (nm) of irregularities is expressed as "the mean value of the spacing between cycles of peaks and valleys obtained from the point where the roughness curve and the mean line cross", and is rendered by the following equation 2.

[equation 2] $Sm = \frac{1}{n}\sum_{i=1}^{n} Smi$

S_{mi} : spacing of irregularities (nm)

n: number of spacings of irregularities within the reference length

It is preferable for the thickness of the tin oxide film or layer (SnO_2) to be from 10 to 800 nm, and for the thickness of the overcoat layer of silicon oxide film (SiO_2) or the like to be from 0.1 to 100 nm.

When the thickness of the tin oxide is less than or greater than this range, the desired irregularities cannot be obtained. That is, deviation outside of this range is not preferable because, when the thickness of the tin oxide is smaller than this range, then a film of uniform thickness will not be realized; and when the thickness of the tin oxide is larger than this range, then the spacing of irregularities will become too large.

A film mainly comprised of common silicon oxide is preferable as the undercoat for the alkali barrier. Additives such as P (phosphorous) and B (boron) may be added, and oxide compounds of tin oxide may be used as needed.

The undercoat film for the alkali barrier may be formed using known processes. Examples include the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, and CVD (chemical vapor deposition) method.

It is preferable that the undercoat film for the alkali barrier be at least 10 nm yet not greater than 300 nm. A thickness less than 10 nm is not preferable because it is insufficient for producing an effective alkali barrier. Additionally, a thickness greater than 300 nm is not preferable because interference colors frequently become noticeable and it becomes difficult to control the optical characteristics of a glass plate.

Glass mainly comprised of silicon oxide (SiO_2), tile, ceramics, or a metal plate is suitable for use

as the substrate. Moreover, a hydrophilic member according to the present invention may be applied to mirrors, for example.

Brief Descriptions of the Drawings

Figures 1(a) and 1(b) are, respectively, enlarged cross-sectional views of hydrophilic members according to the present invention, the member of Fig. 1(b) including an undercoat film not included in the member of Fig. 1(a).

Detailed Description of the Invention

Hereinbelow, explanation will be made of the preferred embodiment of the present invention, based upon the attached drawings.

In the embodiment shown in Figure 1(a), the hydrophilic member comprises a film of tin oxide (SnO_2) 2 formed on the surface of a glass plate 1 as a substrate and a film of silicon oxide (SiO_2) 3 as an overcoat layer formed on the surface of this tin oxide (SnO_2) film 2.

In the embodiment shown in Figure 1(b), an undercoat film 4 stands between the glass plate1 and the tin oxide (SnO_2) film 2 to prevent alkalis such as Na from escaping out of the glass plate 1.

In Figure 1, R_a is the mean surface roughness and Sm indicates the mean spacing of the irregularities.

Soda glass, which has SiO_2 as its main component, is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, CVD (chemical vapor deposition) method, or sputtering method. The thickness ranges from 10 to 800 nm and the mean surface roughness (R_a) ranges from 0.5 to 25 nm. The film of tin oxide (SnO_2) 2 has a rutile structure.

The film of silicon oxide (SiO_2) 3 has a thickness ranging from 0.1 through 100 nm and is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, chemical vapor deposition method, or sputtering method. In addition, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide (SnO_2) film 2 are transferred just as they are, and the range of the mean surface roughness (R_a) of the surface of the silicon oxide (SiO_2) film 3 also becomes within the range of 0.5 to 25 nm.

The mean spacing (S_m) of irregularities preferably ranges from 4 to 300 nm. It is not desirable that the spacing deviate from this range because the long-term stability of the hydrophilic properties is low outside of the range.

By forming minute irregularities on the surface, the hydrophilic properties of the surface can be further improved.

That is, when the surface area becomes larger by r times due to formation of minute irregularities on the surface, $\cos \theta' = r \cos \theta$ ($90° > \theta > \theta'$) is established by Wenzel's formula, in which the contact angle of water at the time of the flat surface is θ and the contact angle of water at the time of forming irregularities is θ'. However, it is not the case when the contact angle θ deviates greatly from 90 degrees.

For example, forming irregularities on the surface of a member having a contact angle of 30° with respect to water when the surface is flat, and taking the surface area to be multiplied 1.1 times, then, from the above equation, $\cos \theta' = 1.1 \cos 30° = 0.935$, and from this it is determined that $\theta' = 17.7°$. Similarly, when the surface area is multiplied by 1.15, θ' becomes 5.2°.

However, this equation is not necessarily established when θ is small, however, as a tendency, θ' becomes smaller by the provisions of irregularities.

That is, by the formation of minute irregularities on the surface, the hydrophilic surface becomes

all-the-more hydrophilic.

On the other hand, as the undercoat film 4 for an alkali barrier, a thin film with silicon oxide as the main component or a compound oxide film comprised of silicon oxide and tin oxide, a film of silicon oxide which includes carbon, or layers of a film with tin oxide as the main components and a film with silicon oxide as the main component, or the like may be used.

For example, a compound oxide film comprised of silicon oxide and tin oxide or a film of silicon oxide which includes carbon has a refractive index which is between that of the glass plate 1 and the tin oxide film 2. Therefore, an even more preferable appearance can be obtained. That is, by having an undercoat film with an intermediate refractive index, it is possible to control interference color changes (color inconsistencies) arising from irregular thickness of the tin oxide film, as well as neutralize reflection hues.

In the case where the undercoat film is a layered body of, for example, a film whose main component is tin oxide and a film whose main component is silicon oxide, because the apparent refractive index of the layered body is between the refractive index of the glass plate 1 and the refractive index of the tin oxide film 2 by adjusting the thickness of the respective films, the functions of the above-mentioned undercoat film with an intermediate refractive index can be obtained.

In the case where the hydrophilic member having the above-mentioned structure is applied to a mirror, a thin film of metal, for example, silver, is formed on the rear surface of the glass plate 1, between the glass plate 1 and the undercoat film 4; or, in the case of no undercoat, between the glass plate 1 and tin oxide (SnO_2) film 2.

Next, explanation will be made of processes for the formation of films occurring with the preferred embodiments of the present invention and comparative examples. Specifically, using a film-forming apparatus (not shown), a sample of embodiment 1 was made by forming, in order, a

film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the samples 2, 3, 4, and 6 of embodiment 2 were formed with, in order, a film of silicon oxide, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the embodiment sample 5 was formed with, in order, a film of tin oxide, a film of silicon oxide, a film of tin oxide, and a film of silicon oxide on the surface of a glass plate.

Using the same process as that of embodiment 1, the sample of comparative example 1 was made with, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. The sample of comparative example 2 was made by conducting an etching process on the surface of an ordinary glass plate, in which the glass plate was immersed into an aqueous solution whose main component was hydrosilicofluoric acid, and on the surface of the glass plate were formed minute irregularities comprised of a porous film whose main component was silica. Using the same process as that of embodiment 1, the samples of comparative examples 4 and 5 were made by forming a tin oxide film on the surface of a glass plate. Comparative example 3 is an ordinary glass plate.

Next, the mean surface roughness (R_a) and the mean spacing (Sm) of the samples of the embodiments and the comparative examples were measured. These values were calculated from profile curves measured with an atomic force microscope (AFM) or an electron microscope.

Furthermore, the samples were washed with bath soap, and changes in the contact angles were measured so that wetting properties of the sample surface with respect to water could be confirmed. The angle of contact with water was measured immediately after washing, after the elapse of 2 hours, and after the elapse of 200 hours.

Tables 1 and 2, below, are, with regards to the hydrophilic member according to the present invention and the comparative examples, comparisons of changes of the contact angles with water

after washing with a detergent.

Table 1

		Embodiment Samples					
		1	2	3	4	5	6
mean surface roughness (nm)		10.0	3.0	7.0	13.0	25.0	8.5
mean spacing (nm)		40	30	65	110	150	70
change of contact angle (°)	immediately after washing	3.0	5.0	4.0	5.0	10.0	4.0
	2 hours after washing	4.0	10.0	6.0	6.0	12.0	6.0
	200 hours after washing	10.0	25.0	15.0	13.0	16.0	14.0
undercoat film composition		--	SiO_2	SiO_2	SiO_2	SnO_2/SiO_2	SiO_2
undercoat film thickness (nm)		--	20	20	20	25/25	20
SnO_2 film thickness (nm)		350	20	250	600	800	300
overcoat film thickness (nm)		20	20	50	20	50	50
remarks							

Table 2

		Comparative examples*				
		1	2	3	4	5
mean surface roughness (nm)		30.0	5.0	1.0	5.0	7.0
mean spacing (nm)		250	45	∞ (infinite)	50	70
change of contact angle (°)	immediately after washing	57.0	14.0	18.0	70.0	78.0
	2 hours after washing	65.0	18.0	20.0	70.0	79.0
	200 hours after washing	68.0	32.0	41.0	73.0	80.0
undercoat film composition		SnO_2/SiO_2	--	--	--	--
undercoat film thickness (nm)		25/25	--	--	--	--
SnO_2 film thickness (nm)		1000	--	--	60	150
overcoat film thickness (nm)		--	--	--	--	--
remarks		*Comparative example 2: glass plate on the surface of which are minute irregularities formed by etching Comparative example 3: ordinary glass plate Comparative example 4: glass plate with a film of tin oxide (SnO_2) provided on the surface Comparative example 5: glass plate with a film of tin oxide (SnO_2) provided on the surface				

Table 1 clearly shows that a hydrophilic member according to the present invention has an angle of contact with water of 10° or less just after washing, and the hydrophilic properties are durable over long periods of time.

On the other hand, Table 2 clearly shows that a common glass plate (comparative example 3) has

an angle of contact with water of about 10° after washing, but the angle of contact gradually increases with time. This may be considered due to hydrophilic durability not being attained since the surface irregularities are small (R_a=1nm). A glass plate with fine irregularities formed on the surface by etching (comparative example 2) also has a contact angle with water of about 10°, but the angle of contact gradually increases with the elapse of time. This is presumably due to durability worsening because the spacing of irregularities is too small in relation to the surface irregularities, and the hydrophilic functions decreasing over time.

Moreover, in the case where the thickness of the tin oxide (SnO_2) film exceeds the range of the present invention (comparative example 1), since the spacing of irregularities on the surface becomes large (S_m > 300 nm), the spacing of irregularities on the surface of the silicon oxide film (SiO_2) becomes large, resulting in hydrophilic properties not able to be attained. Furthermore, when a film of tin oxide (SnO_2) only is formed on a glass plate (comparative examples 4 and 5), the angle of contact with water after washing is 70° or greater and hydrophilic properties are not manifested, regardless of the thickness of the tin oxide film (SnO_2). This is presumably due to the nature of the tin oxide (SnO_2) film itself, regardless of the surface shape.

Embodiment sample 6 is a mirror formed with a film of nearly the same composition as Embodiment sample 3 on the surface of a glass plate having a silvered rear surface, i.e., the film characteristics are all the same, except that the SnO_2 film thickness is 300nm, rather than 250nm. This mirror surface does not fog at all, even when breath is exhaled thereupon, the angle of contact with water becomes 10° or less just after washing, and it maintains hydrophilic properties over long periods. Accordingly, the mirror of embodiment 6 has high hydrophilic properties, and exhibits desirable hydrophilic retention properties.

Industrial applicability

As explained above, according to the first aspect of the above-mentioned hydrophilic member, the angle of contact with respect to water becomes small, allowing still greater long-term stability of hydrophilic properties to be obtained.

According to the second aspect of the above-mentioned hydrophilic member, it is possible to form a polycrystalline film having a desirably irregular surface, while attaining the effects of the above-mentioned first aspect.

According to the third aspect of the above-mentioned hydrophilic member, while attaining the effects of the above-mentioned first and second aspects, hydrophilic effects occurring on the top surface can be sufficiently attained, yet recovery of hydrophilic properties after washing will occur within an extremely short period of time, and the retention of the hydrophilic properties is high.

According to the fourth aspect of the above hydrophilic members, it is possible to maintain hydrophilic properties over a long period of time, while attaining the respective effects of any one of the above-mentioned first, second, or third aspects.

According to the fifth aspect of the above-mentioned hydrophilic member, it is possible to form a desired hydrophilic film while attaining the respective effects of any one of the above-mentioned first through fourth aspects.

According to the sixth aspect of the above-mentioned hydrophilic member, it is possible to obtain desired irregularities while attaining the respective effects of any one of the above-mentioned first through fifth aspects.

According to the seventh aspect of the above-mentioned hydrophobic member, while attaining the respective effects of any one of the above-mentioned first through sixth aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the refractive index of the undercoat film is between the refractive indices of the glass plate and the

tin oxide film.

According to the eighth aspect of the above-mentioned hydrophilic members, while attaining the respective effects of any one of the above-mentioned first through seventh aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the apparent refractive index of the layered film is between the refractive indices of the glass plate and the tin oxide film.

According to the ninth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through eighth aspects, it is possible to make effective applications to mirrors, windshields, anti-fogging/anti-fouling glass for construction, spectacles, lenses, tile, metal plates, and the like.

According to the tenth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through ninth aspects, it is possible to make effective applications to automobile door mirrors, bathroom mirrors, and the like.

Although there have been described what are the present embodiments of the invention, it will be understood by persons skilled in the art that variations and modifications may be made thereto without departing from the gist, spirit or essence of the invention. The scope of the invention is set forth in the appended claims.

What is claimed is:

1. A hydrophilic member comprising:

a tin oxide layer formed on a surface of a substrate; and

an overcoat layer formed on the surface of said tin oxide layer, wherein said overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide, and the mean surface roughness (R_a) of the top surface thereof is within a range of 0.5 to 25 nm.

2. A hydrophilic member according to claim 1, wherein said tin oxide layer has a rutile structure.

3. A hydrophilic member according to claim 1, wherein the mean surface roughness (R_a) of said tin oxide layer is also within a range of from 0.5 to 25 nm.

4. A hydrophilic member according to claim 1, wherein the mean spacing (S_m) of the irregularities of the top surface of said overcoat layer is within a range of 4 nm to 300 nm.

5. A hydrophilic member according to claim 1, wherein said tin oxide layer has a thickness within a range of 10 to 800 nm.

6. A hydrophilic member according to claim 1, wherein said overcoat layer has a thickness within a range of 0.1 to 100nm.

7. A hydrophilic member according to claim 12, wherein the refractive index of said undercoat film acting as a barrier against alkali is between the refractive index of the substrate and the refractive index of the tin oxide layer.

8. A hydrophilic member according to claim 12, wherein said undercoat film is a layered body of tin oxide and silicon oxide.

9. A hydrophilic member according to claim 1, wherein said substrate is selected from the group consisting of: glass the main component of which is silicon oxide; tile; ceramic; and a metal plate.

10. A hydrophilic member according to claim 1, wherein said hydrophilic member is a mirror having a thin metal film formed on the surface thereof, between the substrate and the tin oxide layer.

11. A hydrophilic member according to claim 1, wherein said overcoat layer is formed directly on the surface of the substrate.

12. A hydrophilic member according to claim 1, further including an undercoat film disposed between the surface of said substrate and said tin oxide layer, said undercoat film acting as a barrier against alkali.

13. A hydrophilic member according to claim 12, wherein said hydrophilic member is a

mirror having a thin metal film formed on the surface thereof, between the undercoat film and the tin oxide layer.

14. A hydrophilic member according to claim 2, wherein the mean surface roughness (R_a) of said tin oxide layer is also within a range of from 0.5 to 25 nm.

15. A hydrophilic member according to claim 2, wherein the mean spacing (S_m) of the irregularities of the top surface of said overcoat layer is within a range of 4 nm to 300 nm.

16. A hydrophilic member according to claim 14, wherein the mean spacing (S_m) of the irregularities of the top surface of said overcoat layer is within a range of 4 nm to 300 nm.

17. A hydrophilic member according to claim 2, wherein said tin oxide layer has a thickness within a range of 10 to 800 nm.

18. A hydrophilic member according to claim 15, wherein said tin oxide layer has a thickness within a range of 10 to 800 nm.

19. A hydrophilic member according to claim 16, wherein said tin oxide layer has a thickness within a range of 10 to 800 nm.

20. A hydrophilic member according to claim 2, wherein said overcoat layer has a thickness within a range of 0.1 to 100nm.

Abstract

A hydrophilic member is provided wherein the restoration of hydrophilic properties after washing occurs in an extremely short amount of time, yet the retention effect of the recovered hydrophilic properties is high. On the surface of glass plate, which is used as a substrate, is formed a tin oxide (SnO_2) film, and on the surface of this tin oxide (SnO_2) film is formed, as an overcoat layer, a silicon oxide (SiO_2) film. Soda glass which has SiO_2 as its main component is used as the glass plate. The tin oxide (SnO_2) film is formed, for example, by the chemical vapor deposition method, the thickness of the film being from 10 to 800 nm and the mean surface roughness (R_a) of the surface being from 0.5 through 25nm. Furthermore, the silicon oxide (SiO_2) film is formed by the sputtering method, the thickness being from 0.1 to 100 nm. Moreover, since the silicon oxide (SiO_2) film is formed on the tin oxide (SnO_2) film, the irregularities of the tin oxide film (SnO_2) are transferred just as they are, which makes the silicon oxide (SiO_2) film have a corresponding mean surface roughness (R_a) of from 0.5 through 25 nm.

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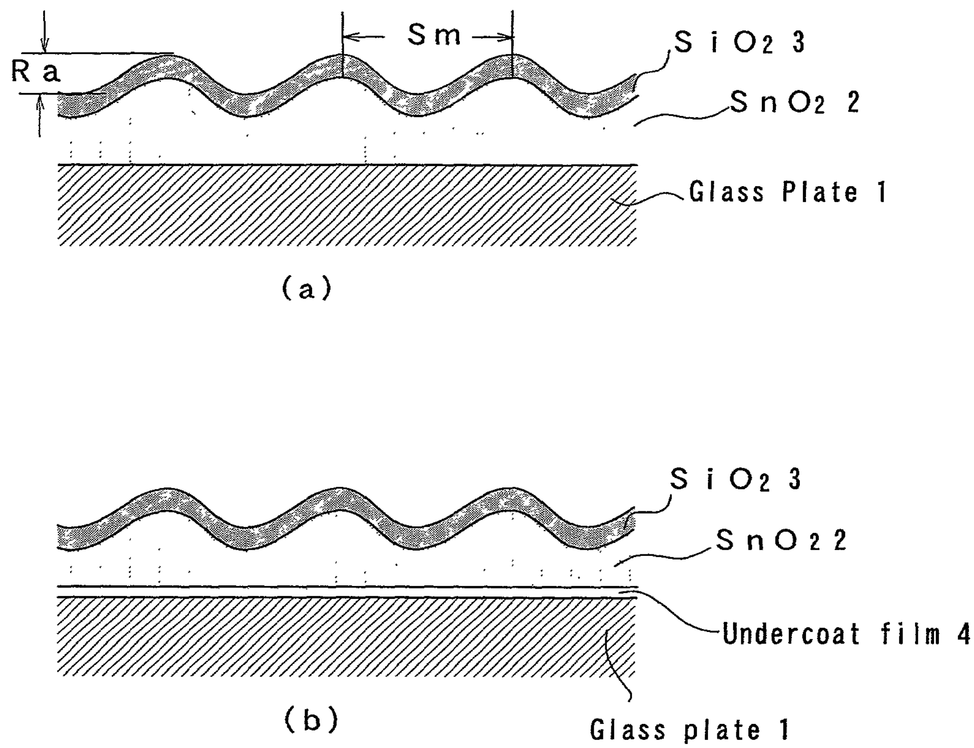
FIG. 1



(a)

(b)

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

HYDROPHILIC MEMBER

上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、

the specification of which is attached hereto unless the following box is checked:

☐ __月__日に提出され、米国出願番号または特許協定条約国際出願番号を__________とし、（該当する場合）__________に訂正されました。

X☑ was filed on 30 November 1999 as United States Application Number or PCT International Application Number PCT/JP99/06675 and was amended on __________ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第３７編第１条５６項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

PTO/SB/106 (8-96)
Approved for use through 9/30/98. OMB 0651-0032
Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Japanese Language Declaration
（日本語宣言書）

私は、米国法典第３５編１１９条(a)-(d)項又は３６５条(b)項に基き下記の、米国以外の国の少なくとも一ヵ国を指定している特許協力条約３６５(a)項に基ずく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)
外国での先行出願

(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願年月日)	Priority Not Claimed 優先権主張なし
10-343688	Japan	03/12/98	☐
11-95014	Japan	01/04/99	☐

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(Application No.) (出願番号)	(Filing Date) (出願日)

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(Application No.) (出願番号)	(Filing Date) (出願日)	(Status: Patented, Pending, Abandoned) (現況：特許許可済、係属中、放棄済)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration
(日本語宣言書)

委任状： 私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。（弁護士、または代理人の氏名及び登録番号を明記のこと）

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith *(list name and registration number)*

Joseph P. Carrier, Reg. No. 31,748; William D. Blackman, Reg. No. 32,397

書類送付先

Send Correspondence to:

CARRIER, BLACKMAN & ASSOCIATES, P.C.
24101 NOVI ROAD, SUITE 100
NOVI, MICHIGAN 48375

直接電話連絡先：（名前及び電話番号）

Direct Telephone Calls to: *(name and telephone number)*

JOSEPH P. CARRIER
248-344-4422

唯一または第一発明者名 1-00	Full name of sole or first inventor Hidefumi FUJIMOTO
発明者の署名 日付	Inventor's signature Hidefumi Fujimoto Date 7. Jun. 2001
住所	Residence Fukuoka, Japan JPX
国籍	Citizenship Japanese
私書箱	Post Office Address c/o TOTO LTD., 1-1, Nakashima 2-chome,
	Kokura-kita-ku, Kita-kyushu-shi, Fukuoka, Japan
第二共同発明者 2-00	Full name of second joint inventor, if any Kazuo TAKAHASHI
第二共同発明者 日付	Second inventor's signature Kazuo Takahashi Date 7. June. 2001
住所	Residence Fukuoka, Japan JPX
国籍	Citizenship Japanese
私書箱	Post Office Address c/o TOTO LTD., 1-1, Nakashima 2-chome,
	Kokura-kita-ku, Kita-kyushu-shi, Fukuoka, Japan

（第三以降の共同発明者についても同様に記載し、署名をすること）

(Supply similar information and signature for third and subsequent joint inventors.)

第三の共同発明者氏名	Full name of third joint inventor, if any Koji TAKEDA
発明者の署名　　日付	Signature　　Date Koji Takeda　　7. Jun. 2001
住所	Residence Fukuoka, Japan　JPX
国籍	Citizenship Japanese
郵便住所	Post Office Address c/o TOTO LTD., 1-1, Nakashima 2-chome,
	Kokura-kita-ku, Kita-kyushu-shi, Fukuoka, Japan
第四の共同発明者氏名	Full name of fourth joint inventor, if any
発明者の署名　　日付	Signature　　Date
住所	Residence
国籍	Citizenship
郵便住所	Post Office Address
第五の共同発明者氏名	Full name of fifth joint inventor, if any
発明者の署名　　日付	Signature　　Date
住所	Residence
国籍	Citizenship
郵便住所	Post Office Address

（第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。）